UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
3608 Hornwood Drive
Houston, Texas 77074

Ray

DATE: 25 MAR 1980

SDS BIOTECH—

SUBJECT: BHC Waste Site at Diamond Shamrock, Green's Bayou Plant

TXD000836486

FROM: Malcolm F. Kallus
Chief, Houston Branch, 6ASA

TO: Oscar Ramirez, Jr., Acting Director,
Surveillance & Analysis Division, 6ASA

As we discussed on March 24, the subject waste site may be worth looking into under RCRA. In our EPA-TWQB Joint Survey Report, dated October 1973, there are several references to and discussions of this site. These include pp. III-11, III-12, III-14, IV-6, and Figure III-1.

I am also enclosing a copy of the company's comments on our report and have marked the pertinent paragraphs.

If you recall, David Hayes of TDWR, District 7 was in to see me and brought out the fact that they are finding BHC in storm water runoff from the plant--so maybe the "impervious clay encapsulated pit" is not so impervious after all. In any case 40 million pounds of BHC isomers is a bunch in anybody's language.

?

Is this site on the Eckhardt list? Or any other list? If not, I think it should be added and looked into from an RCRA standpoint. Let me know what you think.

Mal

Malcolm F. Kallus

Attachments: As Stated

P.S. I'm appalled to hear that your search of the sophisticated R.6 super-duper central filing system proved fruitless in this matter on which we dedicated several years of our lives.

site is on Eckhardt list (#399-2) but not on list of Texas sites to be inspected by EPA

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9792522

Most references to BHC Waste disposal site are marked! See especially Tabs 4, 5, 6, 7, 8

[illegible] 3-25-80

JOINT WASTE SOURCE SURVEY

OF

GALVESTON BAY AND TRIBUTARIES

Field Report on Diamond Shamrock Corporation

(Greens Bayou Plant)

NPDES Appln: No. TX-076-OYV-2-000520

TWQB W.C.O. No. 00749

October 1973

Texas Water Quality Board
District 7

Environmental Protection Agency
Houston Facility

Attachment (1)

I. INTRODUCTION

An intensive survey of the industrial and municipal waste discharges into the Houston Ship Channel is being carried out by combined teams of personnel and facilities from the Texas Water Quality Board (TWQB) and the U.S. Environmental Protection Agency (EPA). This survey was initiated in April 1972 to satisfy the recommendations of the reconvened Galveston Bay Enforcement Conference. The major objectives of this joint survey are to:

1. Examine the quality of the individual wastewater effluents using a more extensive analytical program than has been used previously.

2. Establish baseline data on the total quantity of contaminants currently being discharged into Galveston Bay and its tributaries.

3. Formulate Federal and State permissible discharge limits for each waste source.

4. Establish a schedule of abatement measures necessary to reach the designated limits for each waste contributor.

The latter two objectives are expected to be reflected in the provisions of future State Waste Control Orders and Federal NPDES Permits issued to individual plants. In order to accomplish this, current information on the scope of each plant's operations and waste treatment practices is being collected as a part of the overall survey.

The survey of Diamond Shamrock (Greens Bayou) and other plants included an inspection visit as well as intensive sampling of all effluents. Findings are discussed herein with a review of other pertinent available information, including prior effluent quality measurements and known recent treatability studies.

Texas Water Quality Board	U.S. Environmental Protection Agency
By: Merton J. Coloton, P.E.	By: Malcolm F. Kallus
MERTON J. COLOTON	MALCOLM F. KALLUS
Supervisor	Facility Manager
District 7	Houston Facility, Region VI
Date: November 15, 1973	Date: October 26, 1973

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II. SUMMARY

The following represent the principal findings from the joint survey of the Houston (Greens Bayou) plant of Diamond-Shamrock Company:

1. This plant produces a variety of chlorinated organic chemicals plus organic arsenates and hydrochloric acid. Most of these compounds are used as herbicides (Dachthal and arsenates) or fungicides (Daconil). Hydrochloric acid is produced as a by-product in the manufacture of the chloro-organics.

2. Liquid, sludge, and solid-type wastes generated by this plant are disposed of by several methods. These include (a) discharge of process wastewater into Greens Bayou after neutralization, natural aeration and settling, (b) disposal of concentrated organic wastes plus trash and garbage by commercial waste acceptance firms (c) burial and landfill of waste sludges and solids at in-plant sites.

3. Data obtained during a three day survey (April 3-6, 1973) indicated that the major contaminants discharged by this plant into Greens Bayou, and then into the Houston Ship Channel, are: Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solid (TSS), Oil & Grease (O & G), Arsenate (AsO_4), Chlorinated Hydrocarbons (Cl-HC) and Chlorides (Cl^-).

4. Outfall No. 7 is now the only dry-weather outfall, which includes all the treated wastewater plus much of the plant's storm-water runoff. During the survey, the flow at this outfall averaged 0.37 MGD, compared to the 0.39 MGD monthly average limited specified in the TWQB Waste Control Order (W.C.O.). Survey measured levels of the major contaminants are compard to those established from the monthly average flow and concentration limits specified by the W.C.O., as follows:

(See Table on next page)

	Concentration, mg/l		Load, lb/Day	
	Survey Data	As per W.C.O. of 8/71	Survey Data	As per W.C.O. of 8/71
Flow, MGD	--	--	0.37	0.39
BOD_5	54	100	168	325
COD	420	400	1290	1300
TDS	13,900	51,900	42,800	168,000
TSS	34	100	105	325
O & G	4.5	10	14	32.5
AsO_4	0.21	1.0	0.65	3.25
Cl^-	6,610	7,000	20,400	22,800
Cl-HC	0.7*	--	2.2*	--

* Values shown include Dacthal and Benzene Hexachloride Isomers, only.

The one monthly average limit not being met during the three days surveyed was COD. Chlorinated hydrocarbons were found but are not specifically limited by the present W.C.O. The arsenate level was about 20% of the TWQB specified limit.

5. Bioassay data on the effluent from outfall No. 7 demonstrated that a 100/l dilution of the effluent was toxic to croaker fish. The effluent ditch was observed to be void of any visible algae, plant or animal organisms. Consequently, the present W.C.O. does not appear sufficiently restrictive insofar as insuring that a low toxicity effluent is discharged. Plant personnel contend that effluent toxicity is due primarily to the presence of waste inorganic compounds (e.g., sodium hypochlorite) which have "available" chlorine.

6. Analytical data indicate that arsenates and chlorinated hydrocarbons are probably getting into the effluent from leaching of contaminated surface ditches and a nearby waste burial site.

7. The plant has completed a program to eliminate all dry weather flows from plant ditches, and outfalls other than No. 7. It is still possible that some process wastewater can overflow into these ditches, when rains are large enough to cause overflow of the wastewater collection sumps.

8. At the present time, the plant is permitted by the TWOB to monitor its wastewater effluent at the outlet of the wastewater natural aeration pond(s). Outfall No. 7 is the preferred monitoring location since this would also include any spills, wastewater collection sump overflows and contaminated storm water from the unit process areas.

9. Burial of waste chlorinated organics (and arsenates) is being practiced by this company. Disposal of chlorinated organics by a method (e.g. incineration) that entirely eliminates them from the environment has been arranged for on just an infrequent basis, to date.

III. PLANT PRE-SAMPLING INSPECTION

In order to obtain information needed for the State-Federal Waste Source Survey of the Galveston Bay system, a team of technical personnel from the TWQB and the EPA first visited this Diamond Shamrock plant on 13 July 1972. This visit represented the 15th industrial plant which had been inspected during the joint survey. Subsequent brief visits were also carried out on October 24, 1972 and in 1973 just prior to the sampling portion of the survey.

Information was sought about (1) the plant's current manufacturing operations, (2) current and anticipated waste handling procedures, (3) the nature of the various types of wastes being handled and (4) the locations of the waste water discharge sites. Included herein is a summary of information obtained from plant personnel during the visit and subsequent phone conversations plus personal observations made during the inspection tour.

Attendees present included the following:

Hedley V. Jackson - Plant Technical Manager, Diamond Shamrock
Richard L. Urbanowski - Assistant Plant Manager, Diamond Shamrock
John M. McCann - Process Engineer, Diamond Shamrock
Richard D. Hall - Regional Environmental Control Manager, Diamond Shamrock
LaVern R. Heble - Regional Environmental Control Engineer, Diamond Shamrock
J. L. Thompson, P. E. - TWQB, District 7
S. Clark Allen, Ph.D. - EPA, Dallas
Glenn A. Stankis, P. E. - EPA, Houston

The discussions were held in a conference room at the plant's main office. As requested, the hosts provided each member of the team with a plant map (20 1/2" x 32 1/2"). This map, entitled "Environmental Control Wastewater Plot Plan", (revision of 7/12/72) showed the locations of the plant sewers, ditches, outfalls, etc. in addition to the waste treatment and process areas. Also provided were process flow diagrams for two of the plant's manufacturing operations, which make Dacthal and Daconil pesticides.

Most of the discussion centered on answering a questionnaire prepared especially for this joint survey. After reviewing the questionnaire, the team was escorted on a tour of the plant's waste handling areas and the waste water discharge outfalls.

Manufacturing Operations

Products and Raw Materials

A variety of products are made at this one small plant. The principal products are (a) herbicides, including arsenates and Dacthal (SIC 28184); (b) chloral and chloral hydrate (SIC 28182) and (c) hydrochloric acid (SIC 28194). Also being constructed is a plant to produce Daconil, a fungicide. Estimated startup date for this new plant is November 1, 1973.

The arsenates are produced as both mono-sodium methyl arsenate (MSMA) and di-sodium methyl arsenate (DSMA). The former is sold as a liquid solution while the latter is sold as a solid, having 6 waters of hydration. Except for the hydrochloric acid and arsenates, all products may be considered to be chlorinated organics. Chemical structures for these products are shown in Table III-1.

Raw materials used in the manufacture of the arsenates include arsenic trioxide, methyl chloride, sodium hydroxide, sodium hypochlorite (NaOCl) and dilute sulfuric acid. Byproducts in the process include methanol and the inorganic solids, sodium chloride and sodium sulfate.

According to plant personnel, arsenic in the +3 valence state is much more toxic than the +5 valence state. In the manufacturing process, the starting raw material is in the +3 state, is converted to the +5 state in the initial reactions with sodium hydroxide and methyl chloride, and finally converted back to the +3 state in the final product.

Chloral and chloral hydrate are produced using the raw materials of acetaldehyde, chlorine, concentrated sulfuric acid, 50% sodium hydroxide and water. Byproducts produced include sodium hypochlorite, sodium chlorate ($NaClO_3$), dilute sulfuric acid, and muriatic acid (31 1/2% hydrochloric acid).

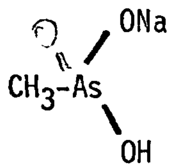
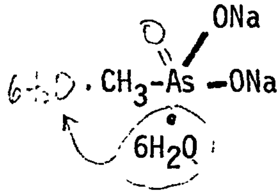
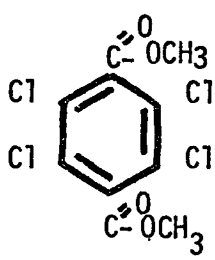
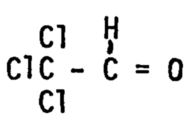
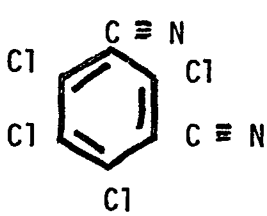
Raw materials used in the manufactur of Dacthal include paraxylene, methanol, chlorine, sodium hydroxide. Also utilized is a ferrous chloride catalyst and a mixed C_8 aromatic solvent. Compounds produced as byproducts include sodium chloride and muriatic acid.

When the DACONIL plant comes on stream, it will be using isophthalyl nitrile, chlorine, carbon tetrachloride and sodium hydroxide as raw materials. Also utilized will be an activated carbon catalyst. Expected byproducts include sodium chlorate, muriatic acid and spent catalyst.

Muriatic acid (31 1/2% HCl) is considered to be a plant product, even though it is produced incidentally in the manufacture of the aforementioned products. It was reported that all the muriatic acid

TABLE III-1

Description of Major Products

Chemical Structure	Trade Name	Use
	Mono-Sodium Methyl Arsenate (MSMA)	Herbicide
	Di-Sodium Methyl Arsenate (DSMA)	Herbicide
	Dacthal	Herbicide
	Chloral	Chemical Intermediate
	Daconil	Fungicide

generated is now being sold. However, there is sporadically generated a large quantity of less than 31 1/2% strength acid, for which there is said to be no market. This low strength acid can be generated at rates of up to 1400 gpd, especially during startup or non-lined out operations of the Chloral and Dacthal units. The plant has chosen to neutralize this acid by converting it to $CaCl_2$ and then wasting it into the Houston Ship Channel rather than (1) concentrate it to the strength of a salable acid solution, (2) convert to a salable solution of $CaCl_2$ used for drilling mud or handle in some other less wasteful manner.

An additional source of contaminated wastewater is the blowdown from the plant's cooling tower. In this system are used various inorganic and organic chemical agents as corrosion inhibitors and inhibitors and algicides.

Processes Having Avoidable Direct Contact with Water

Plant personnel indicated that the use of direct contact cooling (e.g. barometric condensers) was not employed in any of the manufacturing units. However, two instances of a semi-direct contact system were described. One was a steam jet vacuum system in the Dacthal unit. The amount of total process plant wast (H_2O) free basis) associated with this system was estimated to be no more than 1 percent. The other was 3 gpm of seal water used with the vacuum pump in the Dacthal powder packaging plant.

Variability of Plant Operations, Wastewater Flows and Quality

When in operation all units are in production 24 hours a day, continuously. Only the Arsenate unit operates year around, however. The Chloral unit operates in cycles of 1-6 months, mostly in the fall and winter months. Dacthal operations are usually 4-6 months long, once per year. The new Daconil unit is expected to operate about 65% of the time.

The Chloral and Dacthal units currently produce almost all of the wastewater since all of the water at the Arsenate unit, including incident rainfall, is reported to be internally recycled. The one wastewater stream from the Arsenate unit is the "lean" water from the methanol stripping operation. However, this water was reported to be stored at the unit and ultimately used in dilute product formulations.

On a volume basis, one-third of the process wastewater originates from the Chloral unit while two-thirds is from the Dacthal unit.

Wastewater flow and quality usually shows little variation in flow or quality, except due to plant startup and shutdown. The wastewater does go through a large lagoon (Clarifier Pond) before being discharged, which serves to dampen out fluctuations in quality.

At the time of the initial visit, neither the Chloral or Dacthal units were being utilized. Startup times for these two units were scheduled for October 16, 1972, and March 1973, respectively. Operations of the Chloral unit were planned to continue at least through April 10, 1973. For this reason, sampling of the plant's effluent was postponed until April 1973.

Sources of Raw Feed Water for Each Outfall

The plant utilizes water from its own wells at the rate of almost 600,000 gallons per day. About 2/3 of this water, after being used, is discharged - all at the plant's No. 7 outfall. Outfall No. 7 effluent can include a mixture of treated process water, sanitary waste, once-through cooling water, steam condensate and stormwater runoff.

Six other outfalls, 1 through 4/5 plus 6A and 6B, are used for rain water runoff. During each visit, a small continuous flow was observed at outfall No. 4, which was reported to be steam condensate and well-water leakage.

Disposal Procedures For Liquid (& Solid) Wastes

This plant uses several methods for disposal of its organic and inorganic wastes. The principal methods include:

1. Discharge of treated wastewater to Houston Ship Channel via Harris County Flood Control District ditch and Greens Bayou.

2. Depositing of process waste solids and sludges at an in-plant landfill site and in the recent past at a large bural site.

3. Disposal of (a) concentrated organic wastes and (b) trash, garbage, etc. by commercial waste acceptance firms.

At the time of our first visit several "clean" water streams were being bypassed around the treatment system in two ditches, labelled East and West ditches. However, because of an incident occurring in mid 1972, which resulted in excessive arsenic contamination of the combined outfall No. 7 effluent, the plant has been carrying out a program to eliminate all dry weather flows not directed to the waste treatment system. These flows included the following:

a. East Ditch - once through well water used for cooling, and steam condensate.

b. West Ditch - sanitary wastewater plus once through well water used for cooling and seal water on a vacuum pump employed in the Dacthal (solid herbicide) packaging plant.

At the time of the second visit only the program to route the seal water through the treatment system had not yet been completed.

At the time of the sampling (after the first hour), the only other water flowing to the outfall, besides the Clarifier Pond effluent was reported to be leakage from the plant's fire water system. Since the sampling survey, the plant has installed concrete retaining walls (with flood gates) in the East and West ditches to catch accidental spills, etc.

Process Waste Water Treatment (Outfall #7)

The treatment system is basically comprised of neutralization pits plus two parallel ponds that can be classified as settling - oxidation (natural) lagoons or ponds. These Clarifier Ponds were placed into service during the last half of 1971. Incorporated into the collection system are a series of sumps located at each of the individual process units plus a final, large collection sump located adjacent to the neutralizer pits. Thus most of the process wastewater is handled in force mains up to the time that it empties into the ponds. A sketch of this system was furnished by the plant and a simplified version is included as Figure III-1.

The neutralization pits are two beds of dolomitic limestone measuring 200 ft. x 30 ft. x 4 ft. deep. Their purpose is to neutralize spent sulfuric acid as well as any low strength hydrochloric acid generated. Neutralized wastewater was reported to have a pH of 5.5, which corresponded to 7.0 after stripping out the dissolved CO_2.

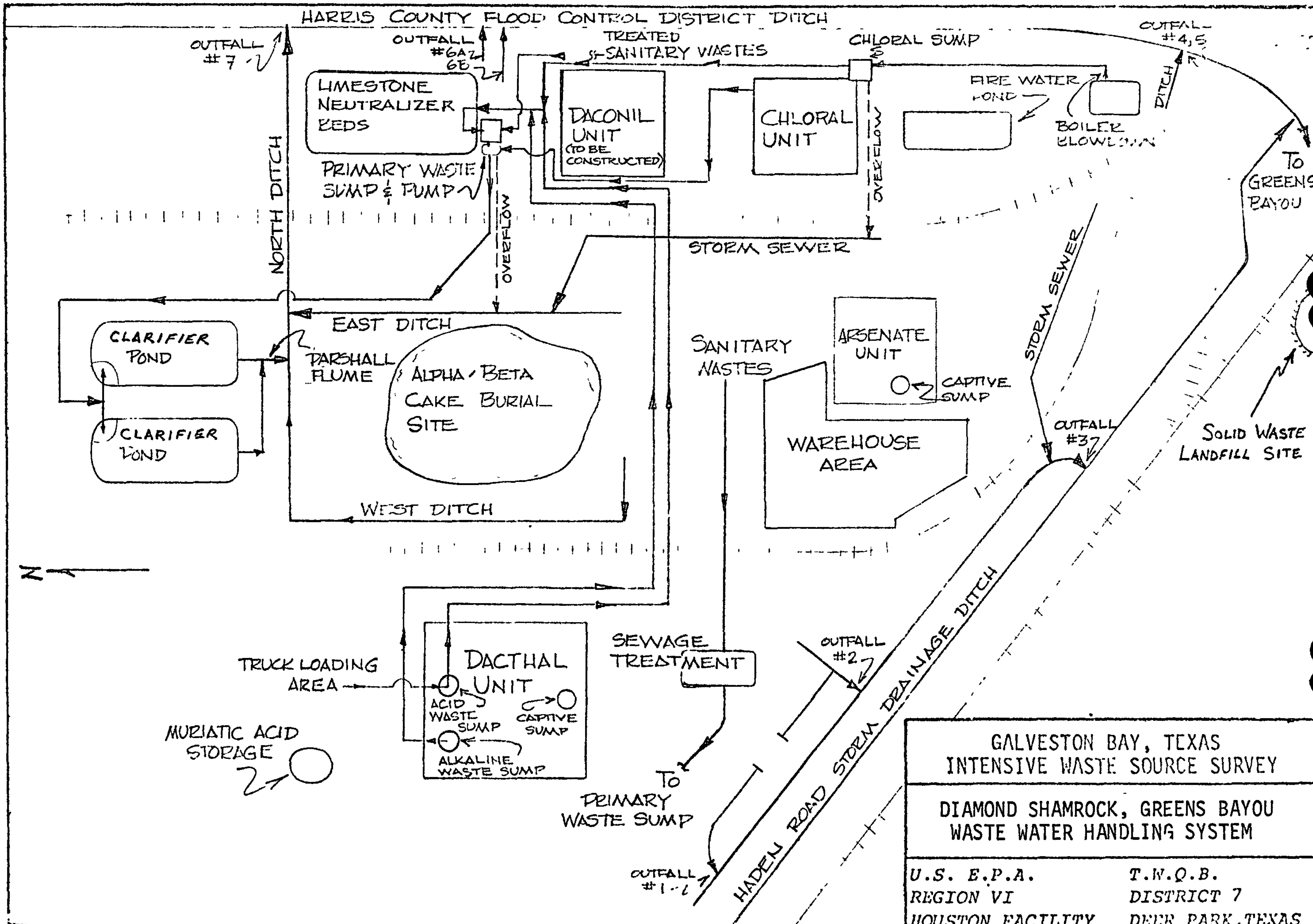
The neutralized streams plus other process wastewater is pumped to one of the two Clarifier Ponds. Theoretical residence time in each of these natural aeration ponds is about 9 days for the typical dry weather flow of 350,000 GPD. These rectangular ponds, with skimmers at the inlet, were constructed so that the inflow could be diverted from one pond to the other if a large spill or some other emergency situation arose. Unfortunately the overall system has several deficiencies.

First, the system is not suitable for removing components included in the wastewater, such as sodium hypochlorite, sodium chlorate or the refractory chloro-organics. Plant personnel contend that effluent toxicity is due primarily to the presence of such compounds as sodium hypochlorite and sodium chlorate, which have "available" chlorine.

Second, the treatment ponds are not designed to insure that the actual retention time is near the theoretical retention time. Short-circuiting is likely since (1) the inlets and outlets are not at opposite corners and (2) there are no baffles in the ponds.

Third, the outlets of each pond are at fixed levels without flow shutoff devices. Therefore, the inactive pond cannot be completely emptied, very readily, in order to maximize its holdup capability. Moreover, the flow in an excessively contaminated active pond cannot be quickly stopped from going to the outfall.

FIGURE III-7



GALVESTON BAY, TEXAS INTENSIVE WASTE SOURCE SURVEY	
DIAMOND SHAMROCK, GREENS BAYOU WASTE WATER HANDLING SYSTEM	
U.S. E.P.A. REGION VI HOUSTON FACILITY	T.W.Q.B. DISTRICT 7 DEER PARK, TEXAS

As mentioned previously, there are a series of collection sumps at the various unit locations. The wastes collected in the Chloral and Dacthal units' sumps are pumped to the treatment system. In case of heavy rains or pump failure, the overflow from these sumps can bypass the treatment system. These overflows are collected in the East and West ditches and then flow to the North ditch leading to outfall No. 7.

All wastewater going to the treatment ponds is ultimately routed through the primary waste sump. This sump also has an overflow into East ditch; however, it was reported that no overflow due to heavy rains had ever occurred. Nevertheless, there still appears to be the possibility of an overflow because the lift pump capacity of the primary sump was reported to be 600 gpm (2-300 gpm pumps), which is only equal to the capacity of the lift pumps (2-300 gpm pump) at just the Chloral unit sump.

Wastewater flow from either of the treatment ponds is measured using a single Parshall Flume equipped with a continuous recorder. The quality of the wastewater is continuously monitored at the exit of the treatment ponds for pH. No other parameters except flow are continuously monitored. Samples can be collected using a newly installed flow proportional compositor. No monitoring is carried out in the primary waste sump - - one reason given was "the corrosive nature of the waste".

Information was sought about the efficienty of the treatment ponds or lagoons for reduction in BOD, COD and TSS. It was reported that influent quality was so variable that a typical level could not be assigned. Typical pond effluent quality was reported to be as follows:

	Concentration (mg/l)	Load (lb/day)
BOD	50	140
COD	300	800
TSS	20	55

The above values correspond to those times when all three of the plants main process units were in operation. That is, lower values are expected when one or more of the manufacturing units are shut down, which is likely to be most of the time.

Consultants used in the design of the treatment ponds were Black, Crow and Eidsness, Inc. Recommended operating procedures for this system were developed and provided by them to Diamond Shamrock.[1]

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1 Letter of June 1, 1971 from Mr. Richard Hall of Diamond Shamrock to Mr. Hugh C. Yantis of Texas Water Quality Board

Stormwater

Rains falling on the concrete padded areas of the process units are routed to the sumps and then pumped to the treatment system. In heavy rains it is possible that the sump pumps cannot handle all the mixed process and stormwater. The overflow is then routed by ditches directly to outfall No. 7, bypassing the treatment system.

One exception to this procedure is the handling of the stormwater at the Arsenate unit. All stormwater falling on the "pad" is reported to be used in the system after collection in the unit sump.

Stormwater falling near but outside of each process unit's concrete padding is not collected but drains into the East and West ditches and then to outfall No. 7.

Several deficiencies in this regard were revealed after a pollution suit was filed against this company by Harris County in 1972. As a result of the company being cited for excessive arsenic concentration in its effluent, an investigation was carried out to determine the probable cause(s).

One of several probable causes was ascribed to the placement of the Arsenate unit waste bin outside the process padded area. As a result, plant instructions were issued to (1) move the bin onto the padded area and (2) improve the housekeeping and spill prevention procedures, especially outside the pad area.

Stormwater falling on the warehouse area is diverted to the East and West ditches by catch basins and storm sewers. According to plant personnel, the accidental loss of arsenate solution from a product drum in the warehouse area in June 1972 may also have been responsible for the higher than normal arsenic content of the outfall No. 7 effluent found by the County on 8/17/72.

As already mentioned, the company has installed concrete retaining walls (with flood gates) in the East and West ditches. The objective is to eliminate effluent contamination due to accidental spills, etc. in the process and materials handling areas.

Another possible source of contaminated stormwater is runoff from the tank car rail sites. This runoff is collected mainly in the East and West ditches also.

Stormwater falling in tank farm and storage areas may or may not be treated depending on the location. Rain falling inside storage tank dikes can be pumped to waste treatment system if desired. That is, if the entrapped stormwater is sampled and a low level of contamination is determined, then it would be drained to a stormwater outfall.

Diking of storage tanks is not utilized in all cases, however. While the raw materials used in Dacthal manufacture, for example, are stored in diked tanks; acid and other, non-flammable product tanks are not diked.

Altogether, this company utilizes six different outfalls for stormwater, in addition to the main outfall, No. 7. These are numbered in Figure III-1 as 1, 2, 3, 4/5, 6A and 6B. As can be seen, these other outfalls are used for stormwater runoff from non-process areas such as parking lots and vacant ground.

Due to the toxic nature of the materials, handled at this plant, consolidation of the stormwater outfalls into a single, monitored discharge seems worthy of serious consideration.

Sanitary Sewage

Sanitary wastes are treated in a small, extended aeration package plant. This plant is a Smith and Loveless unit having a 14,000 gpd design capacity. Chlorination of the effluent is carried out using solid, chlorination tablets of undisclosed composition. The effluent flows thru a chamber containing a stack of tablets, with the flow being proportional to the depth of contact. Dimensions of the tablets are about 3-4 inches in diameter by about 1" thick. The chlorinated effluent is then pumped to the primary waste sump.

Ship's Ballast and Bilge Water

It was reported that the plant has inactive barge facilities and there are no plans to reactivate these. Shipping is carried out primarily in tank cars and tank trucks.

Wastes Sent To Commercial Acceptance Firms

Certain waste materials are removed for handling by commercial waste acceptance firms. It was reported, however, that no wastes are being disposed of using either injection wells or deep sea dumping.

Waste chlorinated and non-chlorinated solvents have been sent to the Rollins-Purle Company. The quantity involved was twenty 55 gallon drums. Frequency was said to be once during the past three years. It was mentioned however that chlorinated hydrocarbons from the Daconil unit will probably also be sent to Rollins-Purle after this new unit starts up in late 1973.

The only other waste materials removed from the plant were reported to be trash and garbage. These materials are hauled off by a contractor, Mobil Waste Service Company.

On-Site Waste Disposal

It was reported that no wastes are being disposed of by in-plant injection wells or in-plant incineration. Techniques utilized are landfilling or burial.

Wastes disposed of on site do include other materials than the dilute (<31%) hydrochloric acid, which is neutralized in dolomitic limestone pits. A total of 10 tons per day of solids is deposited in a crudely diked landfill site (see Figure III-1). Coverage of the waste materials is not carried out on a daily basis; however, and the waste is allowed to pile up.

The majority of the material deposited in this site is inorganic, including sodium chloride, iron chloride and sodium sulfate. Relative amounts of the various materials handled at this site was reported to be as follows:

NaCl	58.2%
Na_2SO_4	34.7%
Chlorinated Hydrocarbons	2.4%
Monosodium Methane Arsenate	0.6%
Iron Chloride	0.3%
Inerts	3.8%

This waste does include some chlorinated, organic chemicals. These are principally intermediates in the manufacture of Dacthal, which are believed to be chlorinated xylenes having an acid group attached. These materials are "filtered out" in the neutralization pit as a slimey deposit, and are then periodically removed for landfilling.

As can be seen, this solid waste does contain some toxic material. Therefore, it is essential that the dike around this site be adequately maintained.

An inactive, burial site for chlorinated hydrocarbons is located at another plant site. It is bounded on three sides by the North, West and East ditches. Buried at this site is approximately 40 million pounds (800,000 cubic feet) of benzene hexachloride (BHC) isomers.

Burial was carried out during the first half of 1971 in a manner approved by the TWQB.

Composition of this material, called "alpha-beta cake", was reported to be as follows:

Alpha isomer of benzene hexachloride	84%
Beta " " " "	7%
Delta " " " "	2%
Gamma " " " "	2%
Other isomers and inorganic material	5%

Only the gamma isomer is the commonly used insecticide, Lindane.

Disposal of chlorinated organics in landfilling operations is not currently considered to be the optimum method of handling this type waste. The more accepted method is in special designed incinerators. Whether to construct its own incinerator or use the services of a suitably equipped commercial waste acceptance firm should, of course, be a company decision.

Anticipated Changes in Treatment of Waste Waters

Because the present facilities were recently put into service, no firm plans have been made to upgrade these. Conversion of the oxidation ponds to mechanically aerated ponds is being considered, if higher degrees of bio-oxidation are required by the regulatory authorities. The prime emphasis however on current activities seem to be on waste prevention rather than waste treatment. It was reported that a study was underway to determine the quality of each waste stream for the purpose of reducing the number of streams needing to be treated.

Observations Plus Samples And Analytical Information Collected

Outfall Description and Waste Water Appearance

The outfall location licensed by the state is considered to be at the outlet of the treatment lagoons or ponds. Unfortunately, at the time of both visits, small flows of wastewater were being bypassed around the treatment system via East and West ditches. Therefore, the total effluent quality and flow was <u>not</u> being measured by the monitoring system.

Even when the plant completes its objective of eliminating all dry weather flows in the East and West ditches, the more inclusive sampling point would be at the discharge end of the North ditch (O.F. #7) rather than the outlet of the settling ponds, where the plant's effluent is currently monitored. This is because of the contamination which has been found to be associated with the stormwater and accidental spills handled by the East and West ditches, and which bypass the effluent treatment and measurement systems.

Wastewater, leaving the West treatment pond, was at a low volume during the time of the visit. Flow rate was 75 gpm and pH was being measured at 7.3. The effluent appeared to be clear and colorless. This was expected since only the Arsenate unit was in service, which does not have a wastewater discharge.

Appearance of Waste Treatment System

Since the system is so elementary, there is little that can go wrong mechanically. The only equipment that was not functioning at the time of the inspection was the automatic, flow-proportioned sampler.

One deficiency observed in the waste treatment pond system was the fixed level of the outlet drain. The problems associated with not being able to vary pond depth in cases of an emergency have already been discussed.

Stormwater Outfalls

All of the stormwater outfalls were dry except one, No. 4/5. There was a flow of heated (~120°F) water equal to about 5 gallons per minute. Plant personnel explained this as being steam condensate plus some well water leaking through an underground pipe into the surface ditch.

A description of all the various stormwater discharge ditches follows:

O.F. #1 - roadside, shallow depression along West side of West parking area which empties into ditch along Haden road.

O.F. #2 - roadside, shallow depression along East side of West parking area which empties into ditch along Haden road.

O.F. #3 - concrete discharge culvert, West of main office which empties into storm drainage ditch along Haden road.

O.F. #4/5 - ditch that drains thru former process outfall structure into Harris County Flood Control District ditch.

O.F. #6A, 6B - two short, ditches located southeast of neutralizer beds, which empty into Harris County Flood Control District ditch.

IV. INTENSIVE WASTE SOURCE SURVEY DATA

Samples were collected of three plant wastewater streams. These included (a) the effluents of outfalls No. 4 and 7 and (b) the treated effluent which was being discharged from the Clarifier Ponds. This latter sample was collected since the self-reporting data collected by the company, as outfall No. 7, includes only the clarifier pond effluent.

Sampling was collected over a three day period during April 3-6, 1973. The weather was dry during these three days except for a light intermittent rain which occurred during the last 6 hours of sampling. At all three sample points, twenty-four hour flow weighted composites were collected for most of the laboratory analyses. Grab samples were obtained for a limited number of chemical and biological tests.

When collecting the 24 hr. composite samples, temperature and pH measurements were made in the field for each aliquot. These aliquots were obtained every 2 hours.

Detailed field and laboratory test data obtained on the three streams sampled are presented in Appendix Tables V-1 through V-7. Also included are the resultant loadings (lb/D) calculated for the various contaminants.

All tests except two were carried out by TWQB and EPA personnel in the EPA Houston laboratory. GC analysis for three types of chlorinated hydrocarbons was carried out by EPA's Pesticide Laboratory in Bay St. Louis, Mississippi. The emission spectrograph analysis was made by a local, commercial laboratory.

Outfall No. 7 Effluent

Measured levels of most contaminants or parameters investigated are presented in Tables V-1, V-2 and V-5 of the Appendix. The major contaminants being discharged into the Houston Ship Channel are: Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Chlorides (Cl^-), Oil and Grease (O & G), Arsenate (AsO_4) and Chlorinated Hydrocarbons (Cl-HC).

Land Fill and Burial Areas

Examination of the Alpha-Beta cake burial site showed no grass growing, although the burial had occurred 1 year previously. Whether this is due to the toxic nature of the covered waste or the poor quality of the top soil is unknown.

Inspection of the landfill site showed sizeable quantities of uncovered chemical wastes. Diking around the site was crude and did not seem adequate to prevent the escape of stormwater during heavy rains.

Waste Handling Facilities Not Examined

Some in-plant waste collection sites were not visually inspected but should be examined in future visits.

These included the following:

1. Arsenate unit captive sump
2. Dacthal unit sumps (3)
3. Barge handling facilities (inactive)

Samples and Analytical Information

A sample of the effluent from the treatment pond was collected for semi-quantitative metals analysis, by emission spectrograph.

Arrangements were made at the time of the visit to obtain a sample of the acclimated "seed" used by the plant for BOD analyses. Diamond Shamrock did provide some of this material for the survey, but it did have to be obtained from Diamond Shamrock's laboratory at their Deer Park plant.

During our inspection visit, plant personnel were asked about chlorinated hydrocarbons being discharged in the effluent. We were informed that some information in this regard had been collected, using an outside testing laboratory - Analytical and Testing Laboratory of Houston. We were then advised that this information could be provided subsequently. This analytical information was requested very recently and the very limited data provided is presented in section IV of this report.

Survey measured levels of these major contaminants are compared to the monthly average limits, specified in or determined from the TWQB Waste Control Order for outfall No. 7, in Table IV-1. At the present time there are no limits specified on chlorinated hydrocarbons. As can be seen from this comparison, the only parameter limit being exceeded at the time of the survey was the concentration of COD. On a lb/D basis; however, the level of COD was not in excess of the W.C.O. limit. The arsenate level was about 20% of the limit specified in the W.C.O.

Biological tests were carried out with this effluent to measure its toxicity. A 48 hour bioassay was carried out using croaker fish (Micropogon Undulatus). A 50% mortality rate (TL_{50}) was produced for wastewater concentrations of $< 1.0\%$. That is, even a 100/1 dilution of the effluent was toxic to this species of marine life. It was also reported by the field crew, which collected the samples, that the effluent ditch was void of any visible algae, plant, or animal organisms. These data indicate that the present W.C.O. limitations are not sufficiently restrictive insofar as insuring that a low toxicity effluent is discharged.

Microbiological testing of the effluent was also carried out to determine the levels of total and fecal coliform present. Measured values per 100 ml. of sample were low and varied between <20 to 1200 for total coliform (with the clarifier pond effluent itself being below the detectable limit of 10 each day). Fecal coliform counts were <10 in all cases.

The identity of the solids present was partially determined. From the data shown in Appendix Tables V-1 and V-5, it is seen that the major constituents were calcium, sodium and magnesium salts. Almost all of these salts are believed to be chlorides, with a small percentage of sulfates.(Dolomitic limestone ($CaMgCO_3$) is used to neutralize waste HCl, etc.)

The result of filtration on effluent quality was found to be limited. BOD_5 and COD contents were lowered 5-10% by laboratory filtration. TOC analysis showed a 20% reduction in the one sample examined. Reductions in the level of heavy metals were indicated to be little, if any.

Organic substances were extracted from a sample of this effluent, so that they could be examined by combined gas chromatography - mass spectrometry (GC/MS). The purpose of this analysis is to determine what specific organic compounds (including but not limited to halogenated hydrocarbons) can be identified in the effluent.

Besides the components identified by EPA's Pesticide Laboratory, other compounds were found to be present including (a) monochloro-xylene, (b) acetophenone, (c) dichloro-xylene and (d) chloroacetophenone. The combined amount of these present was estimated to be about 1 mg/l. Two other compounds indicated to be present but not verified because no standards were available were (a) a dichloropropene and (b) a C_8H_9OCl phenyl compound. The total amount of these compounds present was estimated to be about 1/4 mg/l.

Clarifier Pond Effluent To Outfall No. 7

As mentioned previously, the clarifier pond effluent is 90+% of the effluent discharging through outfall No. 7 in dry weather. During the survey, a limited amount of other wastewater was noted to be flowing to outfall No. 7, but primarily on just the 2nd day of sampling. This additional flow amounted to only about 5% of the combined flow and was reported to be leakage from firewater equipment.

A comparison of certain inspections obtained on the clarifier pond effluent (excerpted from Appendix Tables V-3, V-4 and V-6) and those on the final outfall discharge is presented in Table IV-2.

Comparisons are shown for the individual days as well as for the average of the three day survey. The bioassay data indicated that the treated wastewater leaving the Clarifier Ponds was toxic but not quite as toxic as the effluent leaving the outfall No. 7 sampling point. Diamond-Shamrock personnel contend that effluent toxicity is primarily due to the presence of waste sodium hypochlorite and sodium chlorate, which have "available" chlorine, rather than any product pesticide residues. Nevertheless, the final effluent was indicated to be more toxic than Clarifier Pond effluent.

Corresponding laboratory data did show a higher arsenate content at outfall No. 7 (discharge from North ditch), even when the Clarifier Effluent was the only stream flowing to the outfall. One likely explanation is that the North ditch downstream of the pond discharge point has been contaminated with arsenic, which continually leaches out.

Such a situation was reported to have occurred in 1972. On August 17, 1972, the Harris County pollution control authorities found arsenic levels $>$1.0 mg/l in the final, O.F. #7 discharge. Plant personnel subsequently concluded that some arsenic had accidentally gotten into other ditch(es) that discharge into the North ditch. Two occurrences were cited.

One was the lancing of a drum of arsenate solution, by a fork truck, just ouside Warehouse No. 8. The leaking solution drained into a sewer that emptied into West ditch and was then carried into the North ditch. This accident happened on June 25, 1972, almost two months before the county sampled the effluent. The other likely occurrence was reported to have been contaminated stormwater runoff. Stormwater falling outside the Arsenate Unit pad area, onto land area and/or equipment (e.g. waste bin) contaminated with arsenic, flowed down a stormwater ditch and then combined with Clarifier Pond effluent in the final, North ditch. (See section III of this report for additional information.)

TABLE IV-2

COMPARISON OF CONTAMINANTS IN CLARIFIER POND EFFLUENT AND OUTFALL NO. 7

	Flow MGD	COD lb/D	TOC lb/D	TDS lb/D	TSS lb/D	Cl-HC*, mg/l	Arsenate, mg/l	Toxicity TL_{50} @ 48 Hr.
1st Day								
Pond Effluent	0.350	1211	450	43140	53	--	0.34	1.8%
Outfall No. 7	0.369	1252	523	43170	203	3.2	--	< 1.0%
2nd Day								
Pond Effluent	0.372	1303	465	48320	62	--	0.18	--
Outfall No. 7	0.379	1371	439	46520	63	1.8	0.48	--
3rd Day								
Pond Effluent	0.350	1269	394	39310	67	--	0.11	--
Outfall No. 7	0.350	1246	382	38610	53	1.8	0.82	--
3 Day Average								
Pond Effluent	0.357	1260	435	43590	61	--	0.15ø	1st Day Only
Outfall No. 7	0.366	1290	448	42800	105	2.2	0.65ø	1st Day Only

* Dacthol plus Technical BHC
ø Average of 2nd and 3rd days

TABLE IV-1

LEVELS OF MAJOR CONTAMINANTS IN OUTFALL NO. 7

	Concentration, mg/l		Load, lb/Day	
	Survey Data	As per W.C.O. of 8/71	Survey Data	As per W.C.O. of 8/71
Flow, MGD	--	--	0.37	0.39
BOD_5	54	100	168	325
COD	420	400	1290	1300
TDS	13,900	51,900	42,800	168,000
TSS	34	100	105	325
O & G	4.5	10	14	32.5
AsO_4	0.21	1.0	0.65	3.25
Cl^-	6,610	7,000	20,400	22,800
Cl-HC	0.7*	--	2.2*	--

* Includes Dacthal plus Benzene Hexachloride Isomers only. Others present but not quanitatively determined.

Analysis of the Clarifier Pond effluent for chlorinated organics (e.g. Dacthol, BHC, etc.) was not carried out. Therefore, it is not known whether a sizeable fraction of these contaminants, which appeared at outfall No. 7, were also introduced into the pond effluent after it entered the North ditch. This does seem possible, at least for the BHC isomers.

It was reported that BHC isomers have neither been produced at this plant, directly or as a byproduct, nor used as a raw material in several years. However, the East and West drainage ditches which discharge into the North ditch are located on opposite sides of an extensive burial site for BHC isomers. These were accumulated in earlier years when the pesticide, Lindane, was being produced. BHC isomers are reported to be soluble in water in concentrations of 5-10 mg/l. Therefore, the source of these particular chlorinated hydrocarbons could very well be due to leaching associated with this large, 2 year old burial site.

Diamond-Shamrock reported(1) that a very limited amount of data had been obtained in 1971 on the concentration of chlorinated hydrocarbons in the treated wastewater leaving the Clarifier Ponds. These analyses, which were carried out by a local commercial laboratory, showed that levels were less than 1 mg/l. As is shown in Table IV-2, concentrations measured at outfall No. 7 during the survey were 2-3 mg/l, just for the limited number of compounds included in the laboratory examination.

Comparisons of the analytical data for such contaminants as COD or solids were not indicative of any other measurable differences in the quality of the wastewater leaving the clarifier pond and that being discharged at outfall No. 7.

Outfall No. 4 Effluent

The plant has a TWQB waste control order for only outfall No. 7. All other outfalls are supposed to be just for stormwater runoff. However, during each of the three inspection visits of 1972 and 1973, there was a small flow at the stormwater outfall designated as No. 4 (or 4/5). Plant personnel reported that this stream was only a mixture of steam condensate and well-water leakage; nevertheless, it was decided to include it in the sample survey.

(1) Letter of October 22, 1973, from R. D. Hall of Diamond Shamrock to M. F. Kallus, Houston EPA.

V. APPENDIX

DETAILED LABORATORY AND FIELD DATA

PLUS

CALCULATED EFFLUENT CONTAMINANT LOADINGS

Three Day Joint Waste Source Survey of Diamond Shamrock's

Green's Bayou Plant

Tables V-1 through V-7

Detailed analyses obtained during the three days that this 5 gpm stream was sampled are presented in Tables V-6 and V-7 of the Appendix. These data did not indicate that this stream included any significant levels of those organic or inorganic constituents for which laboratory analyses were carried out. No toxicity problems were indicated by the bioassay test.

Plant personnel did report very recently that the dry weather flow in outfall No. 4 had now been eliminated, by replacing the leaking underground piping.

TABLE V-1

Diamond Shamrock - Green's Bayou

4/3 - 6/73 (3 days)

Outfall #7	1st Day mg/l	1st Day #/D	2nd Day mg/l	2nd Day #/D	3rd Day mg/l	3rd Day #/D	Avg #/D
low (MGD)	0.369	***	0.379	***	0.350	***	0.366MGD
H	6.8	***	6.6	***	6.6	***	6.7 pH
emp (°C)	20	***	20	***	20	***	20° C
OD *	50 *	154	67 *	212	47 *	137	168
OD_F *	--	--	63 *	199	--	--	2nd Day
OD	407	1252	434	1371	427	1246	1290
OD_F	--	--	386	1220	--	--	2nd Day
S	14095	43370	14736	46578	13245	38662	42900
SS	66	203	20	63	18	53	105
SS	10	31	17	54	8	23	36
et'ble Matter (ml/l)		***		***		***	***
OC	170	523	139	439	131	382	448
OC	134	412	--	--	--	--	1st Day
H_3-N	0	0	0.4	1	0.2	0.6	0.5
KN	0	0	0.2	0.6	0.3	0.9	0.5
O_2+NO_3-N	0.6	2	0.7	2	0.7	2	2.0
Ortho PO_4	1.1	3.4	0.79	2.5	0.78	2.3	2.7
-Total, as PO_4	0.72?	2.2?	--	--	0.11?	0.32?	?
il & Grease	9.70@1000	29.8	2.35@0700	7.43	3.6@0700	11	14
	5.02@0700	15.4					
oliform, Total	1200		100	***	< 20	***	***
#/100 ml)Fecal	< 10		< 10	***	< 10	***	***
ioassay TLM,24Hr	1.8%		--	***	--	***	***
,48Hr	< 1.0%		--		--		
henols							
ulfides							
ulfates	200	615	150	474	150	437	509
yanide							
l	6580	20246	6810	21525	6660	19440	20400
-							
r⁻							
d	0.04	.1230	0.13	0.41	0.11	0.32	0.28
d_F	--	--	0.10	0.32	--	--	2nd Day
a	2425	7462	2600	8218	3000	8760	8150
a_F	--	--	2200	6953	--	--	2nd Day
r	0.12	0.3692	0.07	0.2	0.06	0.18	0.25
r_F	--	--	0.05	0.2	--	--	2nd Day
g	0.0016	0.0049	0.0006	0.0019	0.0008	0.002	0.003
g_F	--	--	0.0018	0.0057			2nd Day
s	--	--	0.083	0.26	0.151	0.44	0.35
s_F	--	--	0.091	0.29	--	--	2nd Day
s, as AsO_4	--	--	0.154	0.48	0.280	0.82	0.65
hlorinated Hydrocarbons:							
a.) Dacthol	0.39	1.20	0.50	1.58	0.54	1.58	1.45
b.) Technical BHC	0.64	1.97	0.065	0.21	0.078	0.23	0.80
c.) HCB	0	0	0	0	0	0	0

* Test data indicate a toxicity effect.

TABLE V-2

Diamond Shamrock - Green's B
Outfall #7

DATE: 3-4 April 73

TIME	FLOW (GPM)	pH	°C TEMP
1005	410	7.4	21
1145	240	6.8	22
1350	230	6.7	22
1520	230	6.7	22
1730	230	6.7	20
1925	240	6.7	20
2130	240	6.6	18
2330	250	6.6	18
0130	250	6.8	20
0345	250	6.9	18
0530	250	6.9	19
0720	250	7.0	17
Average	255.8 (=0.369 MGD)	6.8	19.8

DATE: 4-5 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0940	260	6.7	19
1130	260	6.6	20
1330	270	6.8	21
1530	275	6.7	20
1730	270	6.6	20
1925	270	6.6	21
2130	270	6.5	21
2325	250	6.5	19
0125	260	6.7	20
0320	260	6.6	18
0530	260	6.7	18
0725	250	6.7	19
Average	262.9 (=0.379 MGD)	6.6	19.7

DATE: 5-6 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0930	250	6.4	19
1130	250	6.5	21
1335	250	6.6	21
1530	250	6.7	22
1730	240	6.6	22
1940	240	6.5	20
2130	240	6.5	19
2320	240	6.5	19
0120	240	6.7	18
0320	240	6.7	20
0525	240	6.6	19
0720	240	6.7	18
Average	243.3 (=0.350 MGD)	6.6	19.8

TABLE V-3 Diamond Shamrock - Green's B
4/3 - 6/73 (3 Days)

Clarifier Pond Effluent To Outfall No. 7	1st Day		2nd Day		3rd Day		
	mg/l	#/D	mg/l	#/D	mg/l	#/D	Avg #/D
low (MGD)	0.350	***	0.372	***	0.350	***	0.357 MGD
H	6.6	***	6.6	***	6.5	***	6.6 pH
emp (°C)	20	***	20	***	20	***	20 °C.
OD *	53 *	155	63 *	195	45 *	131	160
OD_F *	--	--	70	217	--	--	2nd Day
OD	415	1211	420	1303	435	1269	1260
OD_F	--	--	437	1356	--	--	2nd Day
S	14799	43198	15594	48380	13489	39374	43650
SS	18	53	20	62	23	67	61
SS	8	23	14	43	11	32	33
et'ble Matter (ml/l)		***		***		***	***
OC	154	450	150	465	135	394	435
OC	141	412	--	--	--	--	1st Day
H_3-N	0	0	0.1	0.31	0.1	0.3	0.2
KN	0	0	0.4	1	0.2	0.6	0.5
O_2+NO_3-N	0.7	2	0.7	2	0.8	2	2.0
Ortho PO_4	1.3	3.8	0.83	2.6	0.76	2.2	2.9
-Total, as PO_4	0.18?	0.52?	0.14?	0.43?	0.16?	0.47?	?
il & Grease	8.5@0900	25	3.9@0700	12.1	2.84@0700	8.29	12
	1.7@0700	5.0					
oliform, Total	< 10	***	< 10	***	< 10	***	***
(#/100 ml) Fecal	< 10	***	< 10	***	< 10	***	***
ioassay TLM, 24 Hr.	1.8%	***	--	***	--	***	***
, 48 Hr.	1.8%		--		--		
henols							
ulfides							
ulfates							
yanide							
l	7300	21308	7030	21810	6700	19557	20900
F^-							
r^-							
d	0.08	0.23	0.11	0.34	0.11	0.32	0.29
d_F			0.12	0.37	--	--	2nd Day
Ca	2550	7445	2600	8066	2520	7355	7600
a_F	--	--	3800?	--	--	--	2nd Day
r	0.08	0.23	0.06	0.19	0.06	0.18	0.20
r_F		--	0.05	0.16	--	--	2nd Day
g	0.0008	0.002	0.0006	0.002	0.0008	0.002	0.002
g_F	--	--	0.0014	0.004	--	--	2nd Day
s	0.063	0.184	0.031	0.096	0.020	0.0584	0.113
s_F	--		0.029	0.090	--	--	2nd Day
s, as AsO_4	0.117	0.342	0.058	0.180	0.037	0.108	0.210
OD/BOD		***		***		***	***
OD/TOC		***		***		***	***
OD/TSS		***		***		***	***

* Test data indicate a toxicity effect.

TABLE V-4 Diamond Shamrock - Greens B
Clarifier Pond Effluent to Outfall No. 7

DATE: 3-4 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0945	240	6.6	20
1205	240	6.8	21
1345	230	6.6	21
1520	230	6.6	21
1725	230	6.5	20
1920	240	6.6	20
2120	240	6.5	18
2325	250	6.5	18
0140	250	6.6	18
0330	250	6.7	20
0520	250	6.8	20
0715	250	6.6	19
Average	243 (=0.350 MGD)	6.6	19.7

DATE:4-5 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0930	250	6.6	20
1120	250	6.6	19
1320	260	6.6	21
1525	265	6.6	20
1725	260	6.6	21
1920	260	6.5	21
2125	260	6.4	21
2320	250	6.4	20
0115	260	6.6	19
0315	260	6.5	19
0520	260	6.7	19
0715	250	6.6	20
Average	258 (=0.372 MGD)	6.6	20

DATE:5-6 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0925	250	6.4	20
1120	250	6.4	20
1325	250	6.5	21
1525	250	6.6	22
1720	240	6.5	23
1930	240	6.5	20
2125	240	6.4	20
2315	240	6.4	20
0115	240	6.6	17
0315	240	6.6	19
0515	240	6.6	20
0715	240	6.6	20
Average	243 (=0.350 MGD)	6.5	20.1

TABLE V-5

SEMI-QUANTITATIVE EMISSION SPECTROGRAPHIC ANALYSES*

OF DIAMOND SHAMROCK (GREENS BAYOU) EFFLUENTS ON 4/4-5/73

Element	Approximate Concentration, mg/1 Outfall No. 7	Clarifier Pond Effluent To Outfall No. 7
Aluminum	156	1
Barium	Trace	Trace
Calcium	1426	2000
Chromium	Trace	Trace
Copper	Trace	Trace
Iron	2	0.8
Magnesium	635	482
Strontium	Trace	Trace
Silicon	28	35
Sodium	1329	1175
Vanadium	Trace	Trace
Sulfated Solids∅	13,100	12,900

* By local commercial laboratory.
∅ Solids from ashing sample with H_2SO_4

TABLE V-6

Diamond Shamrock - Greens Bayou
4/5-6/73 (3 Days)
Outfall #4

	4/3-4		4/4-5		4/5-6		
	mg/1	#/D	mg/1	#/D	mg/1	#/D	Avg #/D
'low (MGD)	0.0058	***	0.0072	***	0.0072	***	0.0067 MGD
H	9.1	***	9.0	***	8.9	***	9.0 pH
emp (°C)	22	***	21	***	22	***	22 °C
OD	1	0.05	2	0.12	1	0.06	0.08
OD_F			3	0.18			2nd Day
OD	1	0.05	<1	<0.06	4	0.24	0.1
OD_F							
S	389	18.8	381	22.9	402	24.1	22
SS	0	0	0	0	5	0.30	0.10
SS	0	0	0	0	4	0.24	0.08
et'ble Matter (ml/1)		***		***		***	***
OC	2	0.1	<1	<0.06	<1	<0.06	<0.07
OC	4	0.2	--	--	--	--	1st Day
H_3-N	0	0	0	0	0	0	0
KN	0.4	0.02	0.9	0.05	0.3	0.02	0.03
O_2+NO_3-N	0.1	0.005	0.1	0.006	0.04	0.02	0.01
-Ortho	0.26	0.013	0.04	0.002	0.03	0.002	0.006
-Total	0.4	0.02	0.08	0.005	0.12	0.007	0.011
il & Grease	4.11@0900	0.20	4.96@0900	0.30	2.84@0700	0.17	0.23
	5.68@0700	0.27					
oliform, Total	1500	***	1000	***	3200	***	***
#/100 ml)Fecal	<10	***	20	***	<10	***	***
ioassay TLM, 24 Hr.	>100% @	***		***		***	***
, 48 Hr.	>100% 0900						
henols							
ulfides							
ulfates							
yanide							
l	38	1.8	38	2.3	39	2.3	2.1
-							
r-							
d	<0.01	<0.0005	--	--	--	--	1st Day
d_F							
a							
a_F							
r	0.03	0.002	0.01	0.0006	0.01	0.0006	0.001
r_F							
g	0.0145	0.0007	0.003	0.00018	0.0003	0.000018	0.0003
g_F							
s	0.014	0.0007	0.011	0.0007	0.011	0.0007	0.0007
s, as AsO4	0.026	0.0013	0.020	0.0012	0.020	0.0012	0.0012
b_F Extracted							
OD/BOD		***		***		***	***
OD/TOC		***		***		***	***
OD/TSS		***		***		***	***

TABLE V-7 [redacted] Diamond Shamrock - Green's [redacted]

Outfall #4

DATE: 3-4 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0935	4.0	9.2	22
1120	4.0	9.2	25
1335	4.0	9.2	26
1515	4.0	9.2	25
1720	4.0	9.0	21
1915	4.0	8.8	20
2115	4.0	8.8	20
2320	4.0	8.8	19
0120	4.0	9.0	20
0320	4.0	9.1	19
0515	4.0	9.4	20
0710	4.0	9.4	17
Average	4.0 (=0.0058 MGD)	9.1	21.6

DATE: 4-5 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0920	5	9.1	21
1115	5	9.1	24
1315	5	9.1	25
1515	5	9.0	24
1715	5	8.9	22
1910	5	8.8	20
2120	5	8.8	20
2310	5	8.7	20
0110	5	9.3	19
0310	5	9.3	19
0515	5	8.8	20
0710	5	8.8	20
Average	5 (=0.0072 MGD)	9.0	21

DATE: 5-6 April 73

TIME	FLOW (GPM)	pH	°C TEMP
0915	5	9.1	22
1115	5	9.1	26
1315	5	9.1	27
1515	5	9.0	26
1715	5	8.9	24
1920	5	8.7	22
2120	5	8.7	20
2310	5	8.7	20
0110	5	8.7	20
0310	5	8.8	19
0510	5	8.8	20
0710	5	8.8	20
Average	5 (=0.0072 MGD)	8.9	22.1

See TP 20, 21, page 6 [handwritten initials] 3-25-80

DIAMOND SHAMROCK CHEMICAL COMPANY

A UNIT OF DIAMOND SHAMROCK CORPORATION

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Please Reply to:
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DEER PARK, TEXAS 77536
TELEPHONE 479 2301

February 7, 1974

RECEIVED FEB 8 1974 E.P.A. HOUSTON

For →

Mr. Malcolm F. Kallus
Houston Facility
U. S. Environmental Protection Agency
Region VI
6608 Hornwood Drive
Houston, Texas 77036

Mr. Merton J. Coloton, P. E.
Texas Water Quality Board
2318 Center Street
Deer Park, Texas 77536

SUBJECT: Comments on the Diamond Shamrock Corporation Greens Bayou Plant, Field Report; Joint (EPA-TWQB) Waste Survey; NPDES Appln.: No. TX-076-0YV-2-000570, TWQB No. C0749

Gentlemen:

Your cover letter to the above referenced Field Report requested that we notify you if we "notice any information in this report that would be misleading with respect to the objectives listed in the introduction." After reviewing the Field Report, we have the following comments:

1. The two ponds provided for neutralization (each of these ponds, 30 ft. x 4 ft. x 200 ft.) are interconnected with the main plant wastewater sump, and can serve as surge capacity on the sump in the event of heavy runoff. Utilizing these ponds for surge capacity, we believe the two lift station pumps (300 gpm each) have sufficient capacity to handle the total wastewater flow, even though their capacity is exceeded by the capacity of the process lift stations, which are level controlled. An elbow will be installed on the sump overflow in the near future, to fully utilize this retention capacity.

Attachment (2)

2. Texas Waste Control Order (WCO) No. 00749 specifies the following concentrations for COD: Monthly average - 400 mg/l; 24-hour daily composite - 500 mg/l; and individual sample - 600 mg/l. EPA laboratory data indicates Outfall No. 7, COD averaged 420 mg/l during the three days it was sampled. The data for these three days should be compared to the 24-hour daily composite COD for which the WCO specifies 500 mg/l, and not the monthly average WCO value for COD.

   Additionally, we feel that the EPA laboratory data for COD is incorrect. Our laboratory analyses, conducted in accordance with Standard Methods using HgSO4 to complex chlorides, indicate an average COD of 234 mg/l for split samples with the EPA on the same three days. We might also point out that we have found that the COD procedure recommended by the EPA in its publication, "Methods for Chemical Analysis of Water and Wastes," generally gives even lower values for COD than the Standards Methods Procedure for similar samples.

3. Valves have been installed in the waste stabilization effluent structures which permit draining the ponds to provide emergency retention capacity. However, since the WCO flow limitation is so close to the actual flow, it would be very difficult to drain a pond without exceeding the specified flow limit.

4. We agree that the waste stabilization ponds are subject to short circuiting. During our normal analyses of the pond effluent, we have followed high concentrations of chlorine (about 25 mg/l) through the ponds. We do object to the report authors implying that baffles would improve treatment by reducing short circuiting and increasing retention.

   In our judgement, the main problem with the "ponds" is not short circuiting or spill retention; it is bacterial toxicity due to chlorine. You will note that Diamond did report that the wastes are toxic to fish due to chlorine in the wastes. Normally, 0.1 mg/l of chlorine will kill fish, especially if the chlorine demand of the water has been satisfied and a 0.1 mg/l concentration of chlorine is maintained throughout the fish bioassay. The EPA-TWQB report indicated that the wastes were toxic at a 100:1 dilution, which, in our opinion, represents reducing a 10 mg/l (or higher) chlorine concentration to 0.1 mg/l.

   In our bioassay laboratory work on the Greens Bayou wastewater, we routinely find that the wastewater is toxic to fish, if the chlorine in the wastewater is not neutralized. We normally neutralize these wastewater samples with sodium thiosulfate to determine if the wastewater contains any contaminants other than chlorine, that are toxic to fish. Fish generally survive the bioassay test after chlorine has been removed.

5. The TWQB-EPA report authors note, under the heading, Appearance of Waste Treatment System, that "the waste treatment system is elementary." In our opinion, the simplest system is generally the best, simply because there is less probability of equipment or process failure. We might also point out that the system was performing satisfactorily at the time of the EPA-TWQB survey, producing an effluent quality well within the WCO limits.

6. The discussion contained under the heading, "Samples and Analytical Information," reflects that the EPA-TWQB report authors were disappointed that acclimated seed for the BOD_5 analyses was not maintained at the Greens Bayou Plant. We might remind the report authors that Diamond has three plants in the immediate area, and a fourth under construction, and in the interest of economy and analytical accuracy, Diamond has consolidated its environmental laboratory activities at one location in the area to serve all the plants.

7. The discussion on chlorinated hydrocarbons suggests that Diamond has been negligent in not running detailed analyses and research studies for this undefined and currently unregulated parameter. The chlorinated hydrocarbon data, which was "given" to the EPA, are the results obtained from an outside laboratory. These data were obtained to complete the Corps of Engineers Permit Application. Since the EPA has taken over this permit function, a summary of these data were available to the EPA prior to the time of the survey.

8. The report reflects on the practice of neutralization of weak acid with limestone, as a matter of being wasteful. It also suggests that $CaCl_2$ formed during neutralization, should be concentrated and sold. At best, this is wishful thinking, especially since there is no appreciable market for $CaCl_2$ in any concentration. Concentrating this salt would only be a waste of time, money, and perhaps, a more valuable resource, "energy."

9. The report refers to Arsonate as AsO_4. We believe the correct nomenclature is $AsO_4^{\equiv}$.

For several years the WCO at this Plant has referred to the allowable arsenic concentration as arsonates. The results of laboratory analyses for heavy metals are generally expressed as the metal and not as a radical. Consequently, we feel that this parameter should also be expressed as the metal.

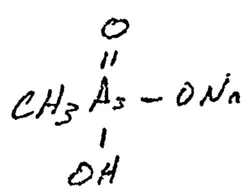
10. The report states, "Burial of waste chlorinated organics (and arsenates) is being practiced by the company. Disposal of chlorinated organics by a method (eg.: incineration) that completely eliminates them from the environment has been arranged for on just an infrequent basis, to date." We find two errors in these statements. The first is that

incineration will not destroy arsenic, and the second, is that we do not generate chlorinated hydrocarbons waste in sufficient quantities to arrange for their disposal on any more than an infrequent basis. This plant currently disposes of chlorinated hydrocarbon waste streams by contract incineration. The only chlorinated hydrocarbons being buried at the active Plant disposal site are traces in waste inorganic salts and spent limestone. We do not feel incineration would be practical for these solid wastes.

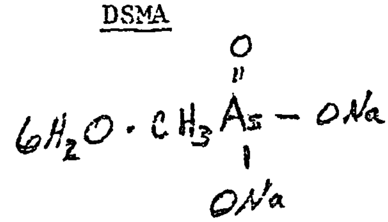
11. The report indicates that arsenic is converted to the +3 valence state in the final product. This is in error, since special precautions are taken to insure that no arsenic products contain arsenic in the +3 valence state. The products are all in the +5 valence state.

12. Table III-1 is in error. The correct chemical structure for MSMA and DSMA are:

MSMA



DSMA



13. The report indicates that the Plant cooling water system blowdown is a source of contaminated wastewater due to corrosion inhibitors and algicides. Please note that we do not use chromates in this system, and that we are willing to consider suggestions for algae, corrosion, and slime control in such a system that would not have any contaminants.

14. The direct contact of 3 gpm of seal water used with the vacuum pump in the DACTHAL powder packaging operation has been discontinued.

15. The report states that: "The wastewater does go through a large lagoon (Clarifier Pond) before being discharged, which serves to dampen out fluctuations in quality." We would like to point out that the ponds also remove both suspended solids and floating matter.

16. The field report states that no monitoring is conducted at the main wastewater sump due to the corrosive nature of the wastes. The pH of the wastewater at this location is checked routinely several times each shift. A composite sampler was once installed at this location, but proved ineffective due to plugging of the sampling equipment with suspended solids. The wastes are corrosive due to chlorine, however, this is not the reason the sampler was removed.

17. The report authors refer to SANURIL 115, used for chlorination in the sewage treatment facility, as "chlorination tablets of undisclosed composition." Please be advised that this product has EPA Registration Number 677-274.

18. Under the heading, "Anticipated Changes in Treatment of Waste Waters," the report authors state that "The prime emphasis, however, on current activities seem to be on waste prevention, rather than waste treatment." We feel that the prime emphasis should always be on waste prevention rather than waste treatment. Since 1970, this Plant has made considerable effort toward wastewater control. These efforts include the following projects: Arsonate Unit Pollution Control, Chloral Unit Effluent Sump, Waste Treatment Improvement (Ponds), Arsonates Methanol Still, DACONIL Manufacturing Chlorine Recovery, Arsonate Packaging Roof, DACTHAL Tankage High Level Alarms, Cooling Water Lines to East Compressor, East and West Ditch Spill Containment Dams, Arsenic Pollution Control, and Lining 350-ft. of East Storm Ditch. In view of these projects since 1970, and other projects being considered, we feel that this section of the report is misleading and does the Plant an injustice.

    As you recall, one of the prime purposes of the existing ponds was to level out the extremes variation of wastewater quality, and to define the character of the wastewater. This work has progressed to the point that we are now considering methods to consistently provide a higher degree of treatment as noted in the Field Report. However, the report authors' statement, "Conversion of the oxidation ponds (Note these ponds are not referred to as clarifier-settling ponds.) to mechanically aerated ponds is being considered, if higher degrees of bio-oxidation are required by the regulatory authorities," was taken out of context. Aeration and mixing will not remove sufficient chlorine from the wastewaters to permit biological activity, and consequently, mechanical aeration will only provide better equalization and possibly reduce suspended solids removal.

19. The report authors imply that the process wastewater monitoring location should be moved from the pond outlet parshall flume to the point where the main plant drainage ditch enters the Harris County Flood Control Ditch. We disagree with the report authors. For several years, the EPA has insisted upon separation of process wastes from stormwater, and now we have made the complete circle. The main Diamond drainage ditch drains some 100 acres of wooded, undeveloped land, in addition to Plant property outside of curbed and diked process areas. During periods of stormwater runoff, the Diamond drainage ditch, as well as the Harris County Flood Control Ditch have been noted to flow bank full. Moving the wastewater monitoring location would only serve to dilute the process wastewater discharge and flood the monitoring location during periods of

heavy runoff.

20. The report authors indicate that the Alpha-Beta cake burial site showed no grass cover, and suggest that the lack of grass may be due to toxicity caused by the material buried. When the Alpha-Beta cake was buried, it was totally encapsulated in a highly impervious clay. We feel that the lack of vegetative growth is caused by poor soil conditions, and not by toxicity.

21. We are not sure whether the second paragraph, under the heading, Land Fill and Burial Areas," refers to the Alpha-Beta cake burial site, or the active Plant solid waste disposal site. If it refers to the Alpha-Beta cake burial site, we disagree in the respect that the waste has been totally encapsulated in clay, and sloped to drain surface water away from the area. If it refers to the active Plant disposal site, we disagree in the regard that the site consists of compacted clay, which slopes to the site. No surface water escapes the active disposal site except by evaporation.

In view of the above comments, and assuming that the appropriate changes are made in the body of the report, we do not believe that the revised body of the report will support the findings given in the summary.

Very truly yours,

LaVern R. Heble, P. E.
Senior Environmental Control Engineer
Texas Registration No. 31147

/bh